

TECHNICAL NOTE

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Characterization of Lachrymators by Ambient Temperature Ion Mobility Spectrometry

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ABSTRACT: Current methods for the detection of tear gas residues require extensive sample preparation before spectral measurement. This contrasts with the present work in which a new detection method for the active ingredients of CN (α -chloroacetophenone), CS (2-chlorobenzylidenemalononitrile), and pepper sprays (capsaicin and crude pepper extracts) based on ambient temperature, atmospheric pressure ion mobility spectrometry has been developed. The minimum determinable limits were: α -chloroacetophenone 0.1 μ g, 2-chlorobenzylidenemalononitrile 25 mg, and cayenne pepper 5 mg. These limits were dependent on the vapor pressure, proton affinity and electronegativity of the target molecule.

KEYWORDS: forensic science, analytical chemistry, tear gas, α -chloroacetophenone, 2-chlorobenzylidenemalononitrile, pepper extracts, ion mobility spectrometry

Aerosol spray cans containing lachrymatory chemicals have increased in popularity in recent years as personal protection devices. Although there are ordinances in many countries prohibiting the carrying of tear gas sprays by members of the general public, their ready availability has seen a concomitant increase in their use during crimes. Acute exposure to the active ingredients of tear gas produces irritation—"burning"—of the skin, eyes, and mucous membranes, coughing, nausea and vomiting. Severe exposure has led to fatalities (1).

The sprays most often encountered by the regulatory authorities in the United Kingdom are the "CN" and "CS" gases. The active ingredient of CN gas is α -chloroacetophenone (Fig. 1, I), CS gas 2-chlorobenzylidenemalononitrile (II), and pepper sprays capsaicin (III) or crude pepper extracts. Published methods for the forensic detection of these compounds include ultraviolet and infrared spectrometry (2), thin layer chromatography (3), and gas chromatography (4,5). However, forensic samples may require extensive separation and purification steps prior to spectral determination. One technique that has the potential to obviate these requirements is ion mobility spectrometry (IMS). Ion mobility spectrometers

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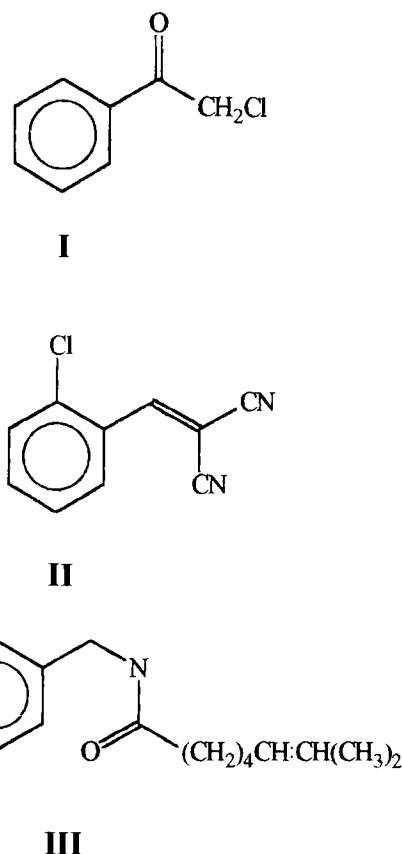


FIG. 1—Chemical structures of α -chloroacetophenone (I), 2-chlorobenzylidenemalononitrile (II), and capsaicin (III).

are small, truly portable devices capable of measuring concentrations of organic chemicals in the vapor phase at the μ g/L level (6). IMS has been known as an analytical technique since the early 1970s. However, only a few specific applications of forensic interest have been reported. These include the detection of explosives (7), narcotics (8), chemical warfare agents (9), and nicotine (10). No detailed studies of tear gas vapors using IMS have been published. In this study a hand-held ion mobility spectrometer was used to characterize the vapors produced at ambient temperature by microgram quantities of α -chloroacetophenone (CN), and by milligram quantities of 2-chlorobenzylidenemalononitrile (CS), capsaicin, and cayenne pepper.

Experimental

Materials—Cyclohexane and capsaicin (Aldrich Chemical Co. Ltd., Poole, UK) were used without further purification. α -Chloroacetophenone (Lancaster Synthesis Ltd., Morecambe, UK) was recrystallized twice from hexane before use. 2-Chlorobenzylidenemalononitrile was prepared by the method of Corson and Stoughton (11) and also recrystallized twice from hexane before use. Cayenne pepper (McCormick Foods, Thame, UK) and cotton wool pads were purchased from a local retail outlet.

IMS System—A hand-held CAM 2 Airborne Vapor Monitor (Graseby Ionics, Watford, UK). Spectra were accumulated using a Graseby Analytical ASP board controlled by the proprietary WASP data acquisition software (Graseby Ionics, Watford, UK).

General Operation—The CAM 2 recycles air through an internal filter system. Some ionization of moisture and oxygen present in this air takes place in the spectrometer ionization chamber (Fig. 2). These ions pass through the drift region under the influence of an electric field, eventually being detected as an ion current. They give rise to a single peak known as the reactant ion peak (RIP, Fig. 3). In purified air, the positive reactant ions are $H^+(H_2O)_2$ and $H^+(H_2O)_3$, and O_2^- the major negative reactant ion (6). In these studies, the positive ion acquisition mode RIP drift time was at 6.5 ms, the negative ion acquisition mode RIP at 6.0 ms.

The introduction of a volatile component into the spectrometer

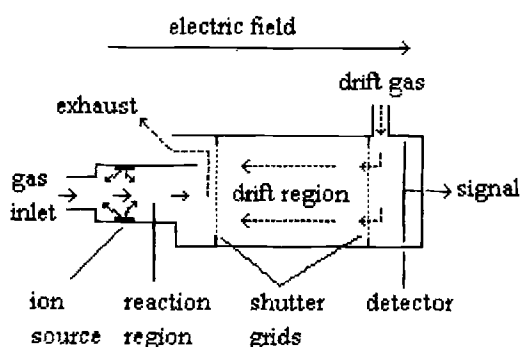


FIG. 2—Simplified diagram of an ion mobility spectrometer.

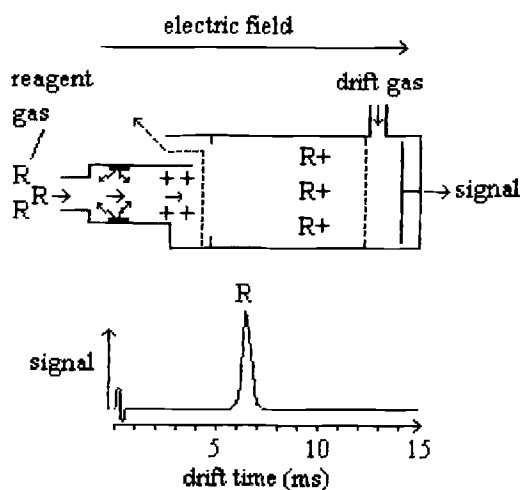


FIG. 3—Generation of IMS reactant ion peak (RIP).

produces additional negative and positive product ions through reactant ion—sample vapor molecule interactions. These too pass through the drift region under the influence of the electric field and, in encountering the counter flow of drift gas, are separated by both charge and size. These ions give rise to spectral peaks at characteristic drift times relative to that of the RIP (Fig. 4). This soft, chemical ionization of sample vapors produces spectra that resemble a total ion chromatogram rather than a fragmentogram, and, as such, they are essentially the vapor phase fingerprints of the target molecules.

General Method—Standard solutions of α -chloroacetophenone were prepared in cyclohexane (this solvent is IMS transparent). The concentrations were such that by injecting 20 μ L of solution onto a cotton wool pad 0.5–50 μ g residues were produced. Due to their poor solubility in cyclohexane and other IMS transparent solvents, 2-chlorobenzylidenemalononitrile, capsaicin, and cayenne pepper were weighed onto the cotton pads. The samples were then placed in 500 mL-round-bottomed flasks, sealed, and left at ambient temperature (20–25°C) for 1 h. Thereafter, the atmosphere inside each flask was sampled by introducing the inlet nozzle of the IMS into the neck of the flask and acquiring data over a period of approximately 30 s.

Results

The method used to prepare and analyze the samples was simple but effective. When sampling the atmosphere inside clean flasks, no depression of the RIP was observed. Cotton wool pads depressed the RIP a little in both ion acquisition modes but did not produce spectra. They were therefore used to mimic the use of swabs or contaminated clothing in forensic investigations.

Spectral Characteristics of α -Chloroacetophenone (I)

Typical α -chloroacetophenone positive ion acquisition mode spectra are shown in Fig. 5. At low residue levels, and hence low vapor concentrations, only the peak at 8.0 ms is consistently observed (Fig. 5a). This peak is probably due to a monomeric molecular ion. This may be a simple cation in which the ketonic oxygen is protonated, or an ion pair produced by S_N1 dissociation of the aliphatic chlorine (12). As the vapor concentration the peak at 11.4 ms, a dimer or clustered dimer species, eventually dominates the spectrum (Fig. 5b). From the plot of peak area against

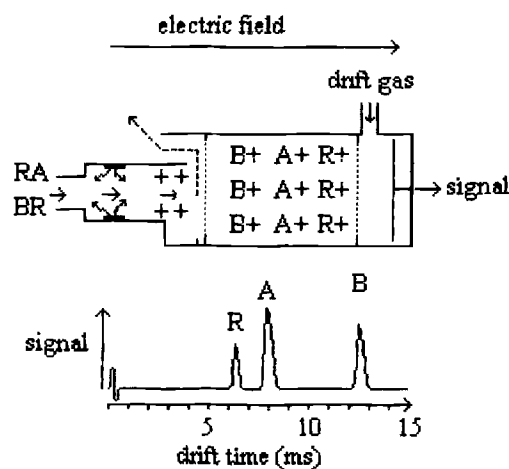


FIG. 4—Generation of IMS spectra.

residue level, the minimum detectable limit (MDL) in the positive ion mode was approximately 0.1 μg .

Typical α -chloroacetophenone negative ion acquisition mode spectra are shown in Fig. 6. The signal at 5.1 ms is due to chloride ion. The molecular ion is at 8.8 ms. No peaks associated with dimeric or cluster ions were observed. From the plot of peak area against residue level, the negative ion mode MDL was estimated to be approximately 1 μg .

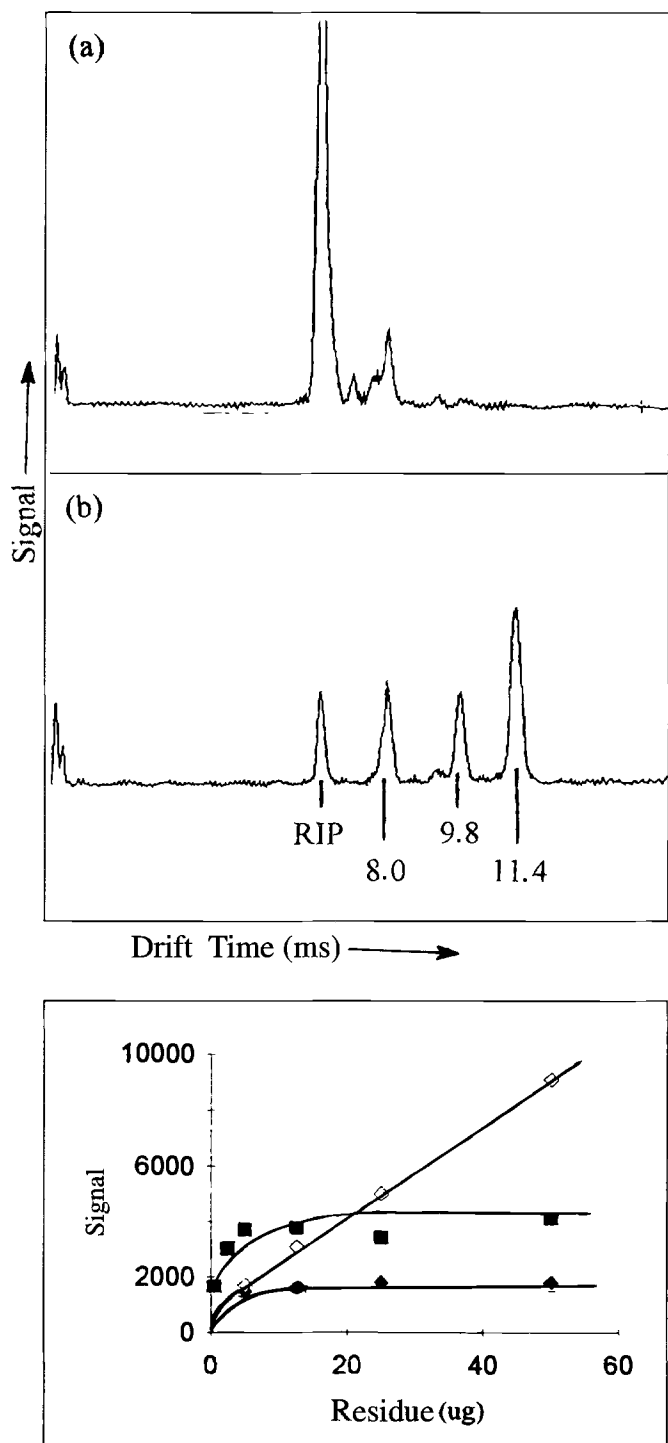


FIG. 5—Positive ion acquisition mode spectra produced by: (a) 1.25 μg , and (b) 50 μg of α -chloroacetophenone. Plot legend: Signal drift time (ms): ■ 8.0, ◆ 9.8, ◇ 11.4

Spectral Characteristics of 2-Chlorobenzylidene-malononitrile (II)

The typical negative ion acquisition mode spectra obtained when sampling the atmosphere above 50 mg of 2-chlorobenzylidenemalononitrile is shown in Fig. 7. The minimum residue level to produce a consistent spectrum was 25 mg. The lack of instrument sensitivity toward 2-chlorobenzylidenemalononitrile may be explained by the low vapor pressure (3.4 by 10⁻⁵ mmHg) and

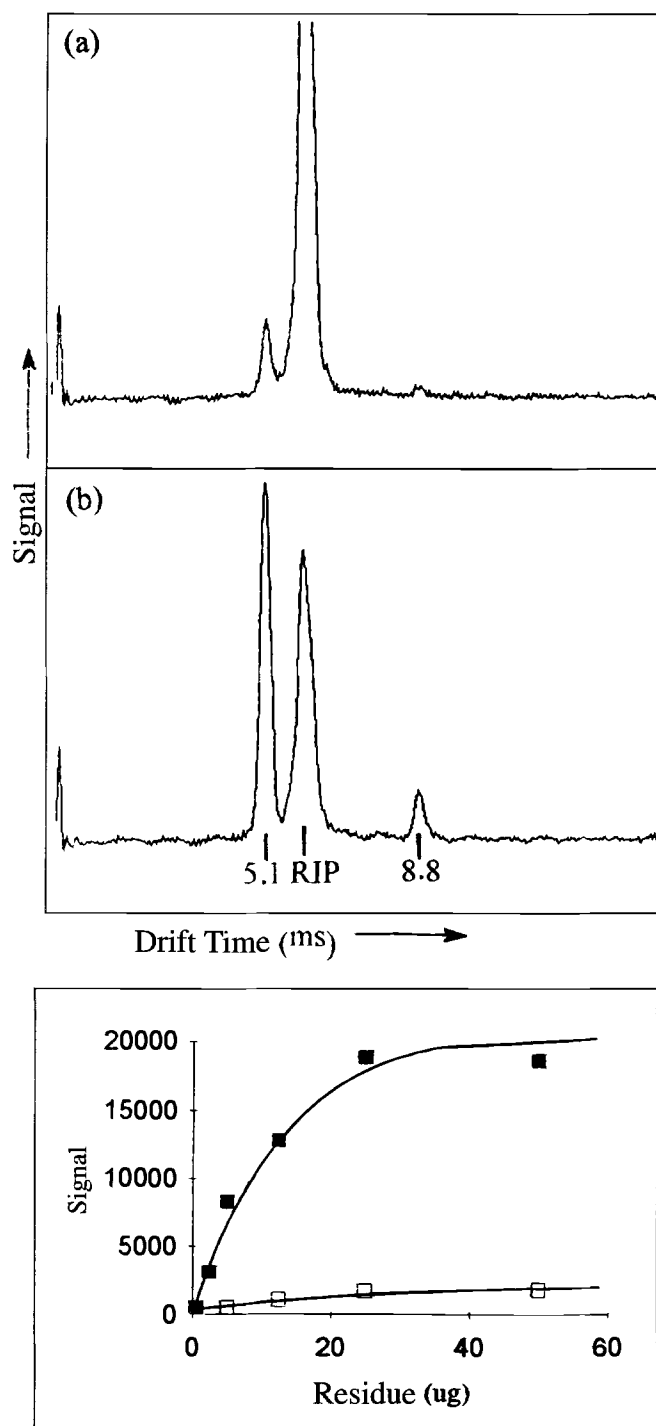


FIG. 6—Negative ion acquisition mode spectra produced by: (a) 1.25 μg , and (b) 50 μg of α -chloroacetophenone. Plot legend: Signal drift time (ms): ■ 5.1, □ 8.8.

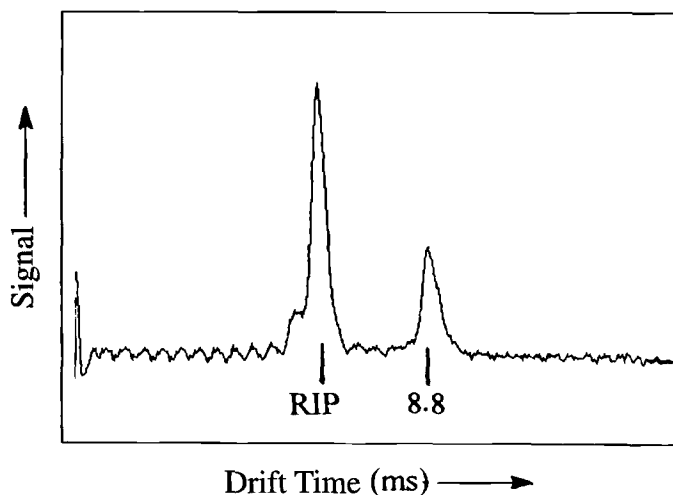


FIG. 7—Negative ion acquisition mode produced by 25 mg of 2-chlorobenzylidenemalononitrile.

reasonably high melting point (95°C) of this compound (*cf.* α -chloroacetophenone, v.p.:5.4 by 10-3 mmHg, m.p.:54–56°C). The 2-chlorobenzylidenemalononitrile spectrum itself is relatively straightforward, consisting of broad molecular ion peak at 8.8 ms. No positive ion acquisition mode spectra were observed.

Spectral Characteristics of Capsaicin (III) and Cayenne Pepper

Capsaicin produced no consistent spectra in either positive or negative ion acquisition modes. The lack of instrument sensitivity may again be explained if capsaicin, although having a relatively low melting point (65°C) and with chemical substituents normally associated with relatively high proton affinity, has an extremely low vapor pressure.

The negative ion acquisition mode spectra characteristically produced by 10 mg of cayenne pepper is shown in Fig. 8. The minimum residue found to produce a consistent spectrum was 5 mg. In this case, it is not capsaicin that is being monitored but some unknown volatile components of the pepper. The exact nature

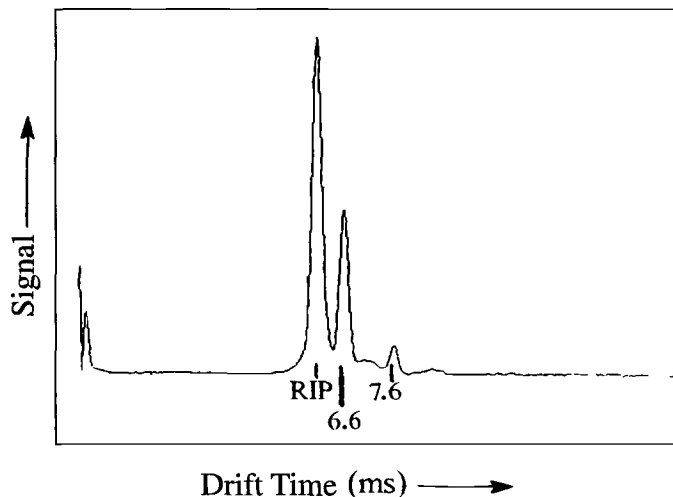


FIG. 8—Negative ion acquisition mode spectra produced by 10 mg of cayenne pepper.

of these components must be determined by IMS/MS. No spectra were observed in the positive ion acquisition mode.

Conclusions

Ion mobility spectrometry can be used to detect the vapors produced at ambient temperature by traces of α -chloroacetophenone, 2-chlorobenzylidenemalononitrile, and cayenne pepper. The minimum determinable limits were dependent on the vapor pressure, proton affinity, and electronegativity of the target molecule. Hence, the difficulty of detecting capsaicin at ambient temperature. This suggests that for complete coverage of the most commonly encountered lachrymators sample pre heating must be used. The ability to obtain spectra in both modes sequentially adds an extra dimension to compound identification. By analyzing first in the negative ion mode, then in the positive it is possible to discriminate between these, and other, compounds. These results suggest that with the further method development this instrumentation will be of value in the rapid screening of scene-of-crime samples and suspect spray cans for these compounds.

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